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FINAL REPORT

IMPROVED FINAL RINSE FOR ZINC PHOSPHATE PRETREATMENT COATINGS

BY

WILLIAM H. DEAVER

MARCH 1971

U. S. ARMY
ABERDEEN RESEARCH & DEVELOPMENT CENTER
COATING & CHEMICAL LABORATORY
Aberdeen Proving Ground
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ABSTRACT

In an effort to increase corrosion resistance of TT-C-490, Type I, zinc phosphate pretreatments a study was conducted on inhibitors added to the final rinse. Salt spray testing and tropical exposure studies indicated that a final rinse containing sodium chromate produced an increase in underfilm corrosion resistance with one coat paint systems.

TABLE OF CONTENTS

I. INTRODUCTION

Tropical exposure of finishing systems for ferrous metals conducted by the US Army Aberdeen Research & Development Center, Coating & Chemical Laboratory (1) showed zinc phosphate coatings, conforming to TT-C-490, Type I, to be the most effective pretreatment. However, a need was shown for improved corrosion inhibition to the metal where the coating system has been damaged. This was illustrated by the rapid failure of the scored areas of specimens exposed at sea coast sites.

Phosphate coatings improve the performance of an organic coating in several ways. It puts the surface in a non-alkaline condition and increases the surface area upon which the system of attracting forces causing adhesion can act. They also inhibit the spread of corrosion from a damaged area to the sound area adjoining it (2). This inhibition is a function of the chromic acid rinse used as a final step in the phosphating process. A certain amount of soluble chromate migrates to areas of rupture in the paint-phosphate film and oxidizes the iron ions of lower valences to ferric oxides and hydroxides followed by the formation of ferric-chromic complexes (3,4).

In view of the role of the final chromic acid rinse in inhibiting corrosion it was decided to study various other inhibitors in the final rinse to determine their effect on the corrosion resistance offered by the zinc phosphate coating.

II. DETAILS OF TEST

Test panels were chosen from one lot of 1010 cold rolled steel. They were sanded, vapor degreased, hand wiped and immersion treated in accordance with Table I using a phosphating material conforming to MIL-P-50002 Type II. The panels were then dried in a forced hot air oven at 180°F. and placed in a dessicator to cool prior to painting. Inhibitors used in the final rinse are listed in Table II.

The panels were painted, using an automatic spray apparatus, to a dry film thickness between 0.9-1.1 mils with lustreless olive drab enamel conforming to Specification TT-E-516, air dried 96 hours and then subjected to 5% salt spray in accordance with Specification TT-C-490. The specimens were removed from the tests when corrosion exceeded that allowed in the specification.

Upon completion of the salt spray tests additional phosphate treated specimens using the most effective rinse were prepared for exposure at the breakwater site in Panama along with standard phosphate treated panels. These were coated with six paint systems representative of various types used by the Army (Table III). The panels were examined for rusting and blistering at the score and general surface condition and rated from 5 to 0 in accordance with Tables IV and V after 6 and 12 months exposure. The paint was then removed and the substrate examined for rusting and pitting and rated in accordance with Table VI.

III. DISCUSSION

Salt spray results are summarized in Table VII. Of the 36 rinses investigated only 8 were equal to or better than the control and of these 8 only sodium chromate showed a substantial improvement. This was apparent at all concentrations. Sodium chromate rinses at concentrations of 0.01, 0.10, and 1.0 percent were therefore selected for further study at the breakwater in Panama.

This site was chosen because its severe environment results in appreciably increased corrosion rates over that in a temperate zone, such as Aberdeen Proving Ground, Md. Exposure at the latter site does not exhibit the rusting and blistering in areas other than the score that appears at the Panama site.

Results of six months exposure in Panama are shown on Table VIII. The sodium chromate rinses showed no improvement over the control rinse with regard to score protection. However, with the 0.10 and 1.00 percent concentrations, there was a definite increase in surface corrosion resistance with both the TT-E-516 and MIL-L-11195 coating systems. This improved corrosion resistance can be seen in Photographs Nos. 1 and 2. This improvement was not shown with TT-E-485 semi-gloss enamel, photo 3, and the two coat paint systems. While the surface condition of the panels prepared with the low (0.01%) concentration rinse was comparable to the control it did show a tendency to be less effective at the score. The same trends were also shown after 12 months exposure (Table IX).

Since the effectiveness of the rinse improved with increased concentration of sodium chromate another set of panels were prepared using a rinse with 2% sodium chromate. These were coated with TT-E-516, MIL-L-11195 and TT-E-485 and exposed in Panama. After 6 months exposure corrosion resistance of the 2.0% concentration was not significantly better than the 1.0% concentration (Table X).

IV. CONCLUSION

This work has shown that sodium chromate used as a final rinse in a TT-C-490, Type I procedure offers increased substrate corrosion resistance with one coat paint systems. It is recommended that consideration be given to raising the pH requirement for the final chromic rinse of TT-C-490, Type I, to permit the use of sodium chromate.

V. REFERENCES

1. Sandler, Melvin H., Tropical Exposure of Finishing Systems for Ferrous Metals, USAARDC, Coating and Chemical Laboratory, Report No. 197.

2. Metal Finishing Guidebook Directory, 1970 Edition, Metals and Plastics Publications, Inc., Westwood, New Jersey.

3. Reed, A. B., Effect of Chromic-Phosphoric Acid Rinses on Performance of Phosphate Coatings, Development and Proof Services, Aberdeen Proving Ground, Laboratories Report No. 8.

4. Evans, Ulick R., Metallic Corrosion Passivity and Protection, Edward Arnold and Company, London, 1948.

APPENDIX A

TABLE I

TT-C-490, Type I, Procedure

Step 1 - Vapor degrease and hand wipe.

Step 2 - Immerse 5 minutes in following bath:

MIL-P-50002, Type II	- 950 ml
Water (to make)	- 13 gals
Total Acid	- 20 points*
Free Acid	- 4 points**
Temperature	- 190°F

Step 3 - Water rinse 60 seconds at room temperature

Step 4 - Immerse in final inhibitive rinse 60 seconds at 150°F.

*1 point = 1 ml of 0.1 N NaOH titrating a 10 ml bath sample to a phenolpthalein end point.

**1 point = 1 ml of 0.1 N NaOH titrating a 10 ml bath sample to a methyl orange end point.

TABLE II

Inhibitors Used as Final Rinse

Inhibitor	Concentration, % by Weight
Chromic-Phosphoric Acid (Control)	50-50 mixture at 4 oz/100 gal
Potassium Ferrocyanide	0.01
Potassium Ferrocyanide	0.10
Potassium Ferrocyanide	1.00
Potassium Dichromate	0.01
Potassium Dichromate	0.10
Potassium Dichromate	1.00
Sodium Chromate	0.01
Sodium Chromate	0.10
Sodium Chromate	1.00
Potassium Permanganate	0.01
Potassium Permanganate	0.10
Potassium Permanganate	1.00
Sodium Phosphate, Monobasic	0.01
Sodium Phosphate, Monobasic	0.10
Sodium Phosphate, Monobasic	1.00
Hydroxyquinoline	0.01
Hydroxyquinoline	0.10
Hydroxyquinoline	1.00
Nickle Nitrate	0.01
Nickle Nitrate	0.10
Nickle Nitrate	1.00
Sodium Tetraborate	0.01
Sodium Tetraborate	0.10
Sodium Tetraborate	1.00
Stannous Sulfate	0.01
Stannous Sulfate	0.10
Stannous Sulfate	1.00
Stannous Chloride	0.01
Stannous Chloride	0.10
Stannous Chloride	1.00

TABLE II - Continued

Inhibitor	Concentration, % by Weight
Stannous Fluoborate	0.01
Stannous Fluoborate	0.10
Stannous Fluoborate	1.00
Potassium Stannate	0.01
Potassium Stannate	0.10
Potassium Stannate	1.00

TABLE III

Organic Coatings Used for Tropical Exposure Test

1. TT-E-516 - Enamel, Lustreless, Quick-Drying, Styrenated Alkyd Type
2. MIL-L-11195 - Lacquer, Lustreless, Hot Spray
3. TT-E-485 - Enamel, Semi-Gloss, Rust-Inhibiting
4. TT-P-664 - Primer, Coating, Synthetic, Rust-Inhibiting, Lacquer-Resisting
   TT-E-516 - Enamel, Lustreless, Quick-Drying, Styrenated Alkyd Type
5. MIL-P-11414 - Primer Coating; Lacquer, Rust-Inhibiting
   MIL-L-11195 - Lacquer, Lustreless, Hot Spray
6. TT-E-485 - Enamel, Semi-Gloss, Rust-Inhibiting
   TT-E-485 - Enamel, Semi-Gloss, Rust-Inhibiting

Systems number 1, 2 and 3 applied at 1 mil dry film thickness.

Systems number 4, 5 and 6 - primer applied at 1 mil dry film thickness and topcoat applied at 1 mil dry film thickness.

TABLE IV

Rating of Score

Score Condition

Rating	Rusting and/or Blistering
5	None - 1/32 inch
4	1/32 - 1/16 inch
3	1/16 - 1/8 inch
2	1/8 - 3/16 inch
1	3/16 - 1/4 inch
0	- 1/4 inch

Undercutting at Score

Rating	Rusting and/or Blistering
5	None - intermittant
4	Continuous to 1/16 inch
3	Continuous 1/16 - 1/8 inch
2	Continuous 1/8 - 3/16 inch
1	Continuous 3/16 - 1/4 inch
0	Continuous - 1/4 inch

TABLE V

Rating of Surface

Surface Condition*

Rating	A. Rusting Alone (Corrosion)
5	None
4	ASTM Photo No. 10, Type I
3	ASTM Photo No. 9, Type I
2	ASTM Photo No. 8, Type I
1	ASTM Photo No. 7, Type I
0	ASTM Photo No. 6, Type I or worse

Rating	B. Rusting Accompanied by Blistering
5	None
4	Trace, less than 5 defects on 4x12 inch panel
3	ASTM Photo No. 8, Type 2
2	ASTM Photo No. 7, Type 2
1	ASTM Photo No. 6, Type 2
0	ASTM Photo No. 4, Type 2 or worse

Rating	C. Blistering Alone
5	None
4	Trace, ASTM Blister Size 2 on 4x12 inch panel - 2 max ASTM Blister Size 4 on 4x12 inch panel - 4 max ASTM Blister Size 6 on 4x12 inch panel - 6 max ASTM Blister Size 8 on 4x12 inch panel - 8 max
3	ASTM Few - Record blister size
2	ASTM Medium - Record blister size
1	ASTM Med-Dense - Record blister size
0	ASTM Dense - Record blister size

*Select applicable condition.

TABLE VI

Rating of Substrate

Substrate Condition

Rating	Pitting and/or Corrosion Spots
5	None
4	Trace - ASTM Blister size 2 on 4x12 inch panel - 2 max ASTM Blister size 4 on 4x12 inch panel - 4 max ASTM Blister size 6 on 4x12 inch panel - 6 max ASTM Blister size 8 on 4x12 inch panel - 8 max
3	ASTM Few - Record size
2	ASTM Medium - Record size
1	ASTM Med-Dense - Record size
0	ASTM Dense - Record size

TABLE VII

5% Salt Spray Exposure

Rinse	Conc., % by Weight	Hours to Failure	Score	Surface	Substrate
Chromic-Phosphoric Acid (Control)	0	192	4	B3	3
Potassium Ferrocyanide	0.01	72	3	B2	2
Potassium Ferrocyanide	0.10	120	3	B3	3
Potassium Ferrocyanide	1.00	72	3	B2	2
Potassium Dichromate	0.01	192	4	B3	2
Potassium Dichromate	0.10	216	4	B3	2
Potassium Dichromate	1.00	216	4	B3	2
Sodium Chromate	0.01	312	4	B3	3
Sodium Chromate	0.10	312	4	B3	3
Sodium Chromate	1.00	312	4	B3	3
Potassium Permanganate	0.01	96	3	B3	2
Potassium Permanganate	0.10	96	3	B3	2
Potassium Permanganate	1.00	Too powdery to paint			
Sodium Phosphate, Monobasic	0.01	144	3	B3	2
Sodium Phosphate, Monobasic	0.10	144	3	B3	2
Sodium Phosphate, Monobasic	1.00	144	3	B3	2
Hydroxyquinoline	0.01	72	3	B3	2
Hydroxyquinoline	0.10	168	3	B3	2
Hydroxyquinoline	1.00	Too powdery to paint			
Nickle Nitrate	0.01	144	4	B3	3
Nickle Nitrate	0.10	144	4	B3	3
Nickle Nitrate	1.00	192	4	B3	3
Sodium Tetraborate	0.01	72	4	B3	2
Sodium Tetraborate	0.10	72	4	B3	2
Sodium Tetraborate	1.00	72	4	B3	2
Stannous Sulfate	0.01	72	4	B2	2
Stannous Sulfate	0.10	72	4	B2	2
Stannous Sulfate	1.00	72	4	B2	2
Stannous Chloride	0.01	72	4	B2	2
Stannous Chloride	0.10	72	4	B2	2
Stannous Chloride	1.00	72	4	B2	2

TABLE VII - Continued

Rinse	Conc., % by Weight	Hours to Failure	Score	Surface	Substrate
Stannous Fluoborate	0.01	144	4	B3	2
Stannous Fluoborate	0.10	144	4	B3	3
Stannous Fluoborate	1.00	144	4	B3	3
Potassium Stannate	0.01	144	4	B3	2
Potassium Stannate	0.10	144	4	B3	3
Potassium Stannate	1.00	144	4	B3	3

TABLE VIII

6 Months Exposure at Breakwater Site, Panama

	TT-E-516			MIL-L-11195			TT-E-485		
	Score	Panel	Substrate	Score	Panel	Substrate	Score	Panel	Substrate
CrO_3-H_3PO_4	4	B0	2	3	B3	2	3	B4	3
0.01% CrO_4	3	B3	2	3	B3	2	0	B4	3
0.10% CrO_4	4	B3	3	3	B4	3	3	B4	3
1.00% CrO_4	4	B3	3	3	B4	3	3	B4	3

	TT-P-664 & TT-E-516			MIL-P-11414 & MIL-L-11195			TT-E-485 & TT-E-485		
	Score	Panel	Substrate	Score	Panel	Substrate	Score	Panel	Substrate
CrO_3-H_3PO_4	4	5	5	3	C4	4	2	5	5
0.01% CrO_4	4	5	4	3	5	4	2	5	5
0.10% CrO_4	4	5	4	3	5	4	3	5	5
1.00% CrO_4	4	5	4	3	5	5	2	B4	4

TABLE IX

12 Months Exposure at Breakwater Site, Panama

	TT-E-516			MIL-L-11195			TT-E-485		
	Score	Panel	Substrate	Score	Panel	Substrate	Score	Panel	Substrate
CrO_3-H_3PO_4	2	B0	0	0	B0	0	1	B2	2
0.01% CrO_4	1	B0	0	0	B0	0	0	B0	0
0.10% CrO_4	3	B0	1	0	B0	0	3	B2	2
1.00% CrO_4	3	B0	2	1	B0	1	1	B4	3

	TT-P-664 & TT-E-516			MIL-P-11414 & MIL-L-11195			TT-E-485 & TT-E-485		
	Score	Panel	Substrate	Score	Panel	Substrate	Score	Panel	Substrate
CrO_3-H_3PO_4	3	B4	4	2	5	5	3	5	4
0.01% CrO_4	3	5	4	2	5	5	2	5	4
0.10% CrO_4	2	A4	3	1	A4	4	2	A4	4
1.00% CrO_4	2	5	4	0	5	4	0	5	4

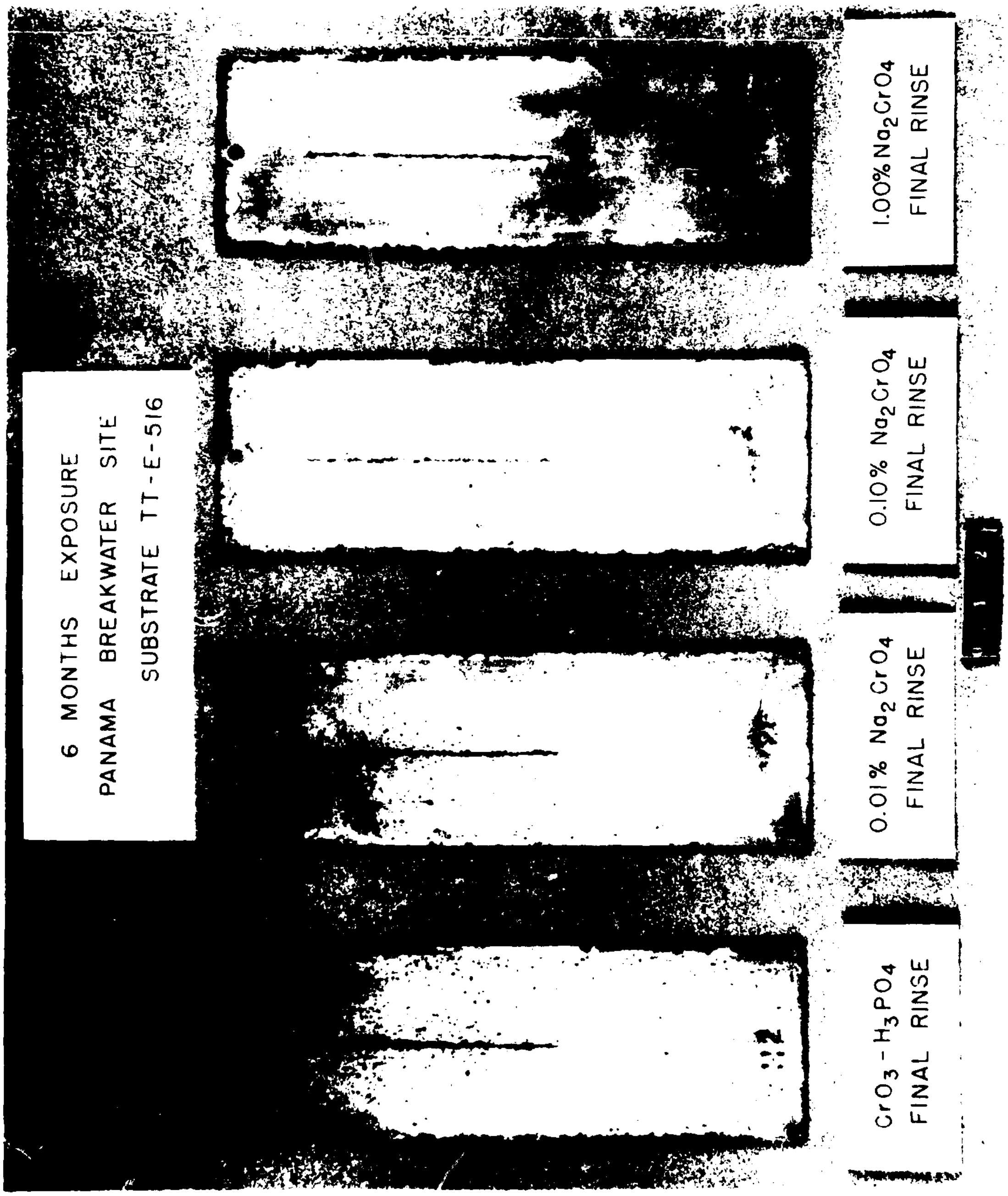
TABLE X

Six Months Exposure at Breakwater

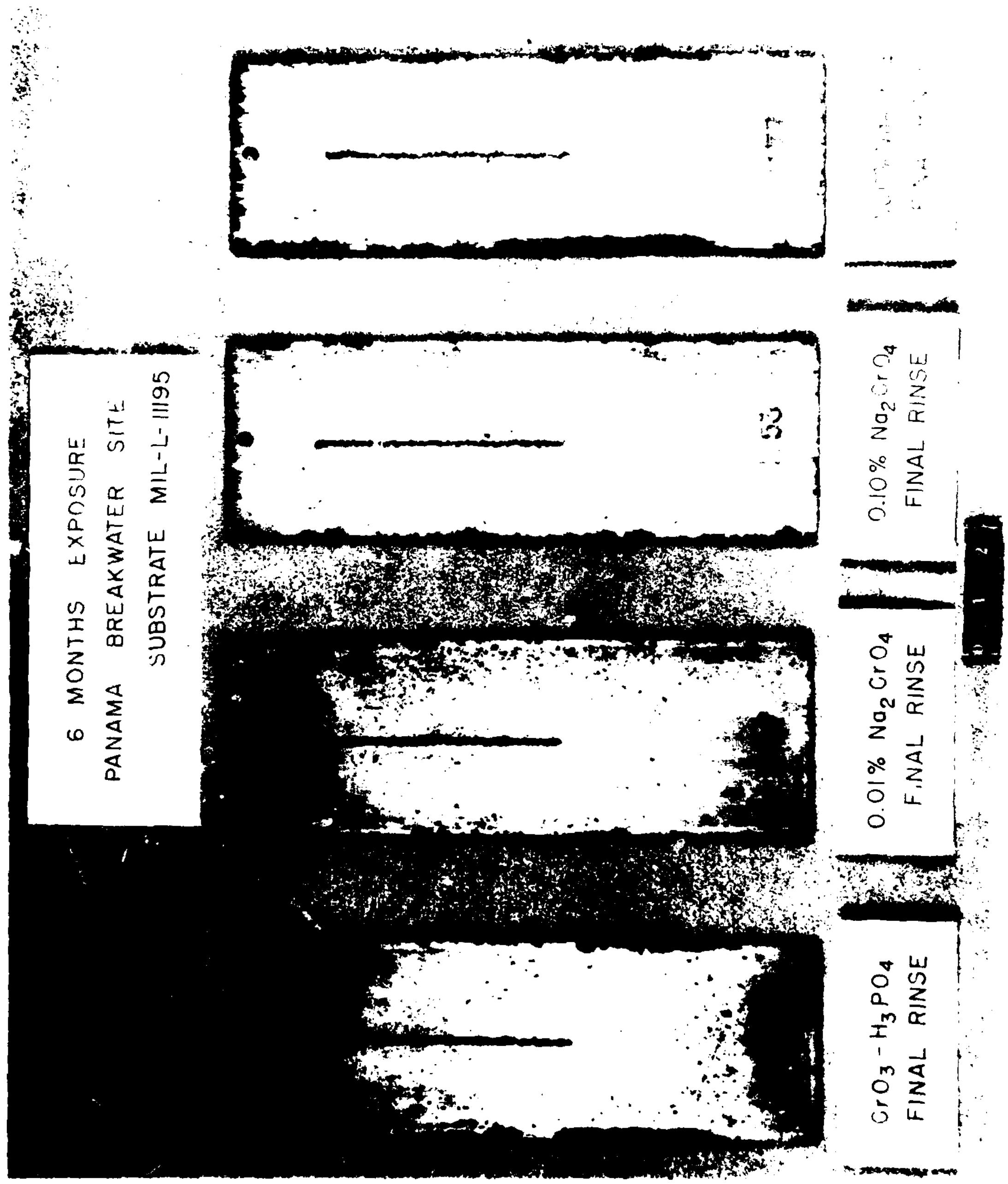
	TT-E-516			MIL-L-11195			TT-E-485		
	Score	Surface	Substrate	Score	Surface	Substrate	Score	Surface	Substrate
Chromic-Phosphoric	4	A0	1	4	A2	1	3	A1	2
Sodium Chromate 1.00%	4	A0	2	4	A4	3	3	A1	1
Sodium Chromate 2.00%	4	A1	3	4	A4	3	3	A2	2

APPENDIX B

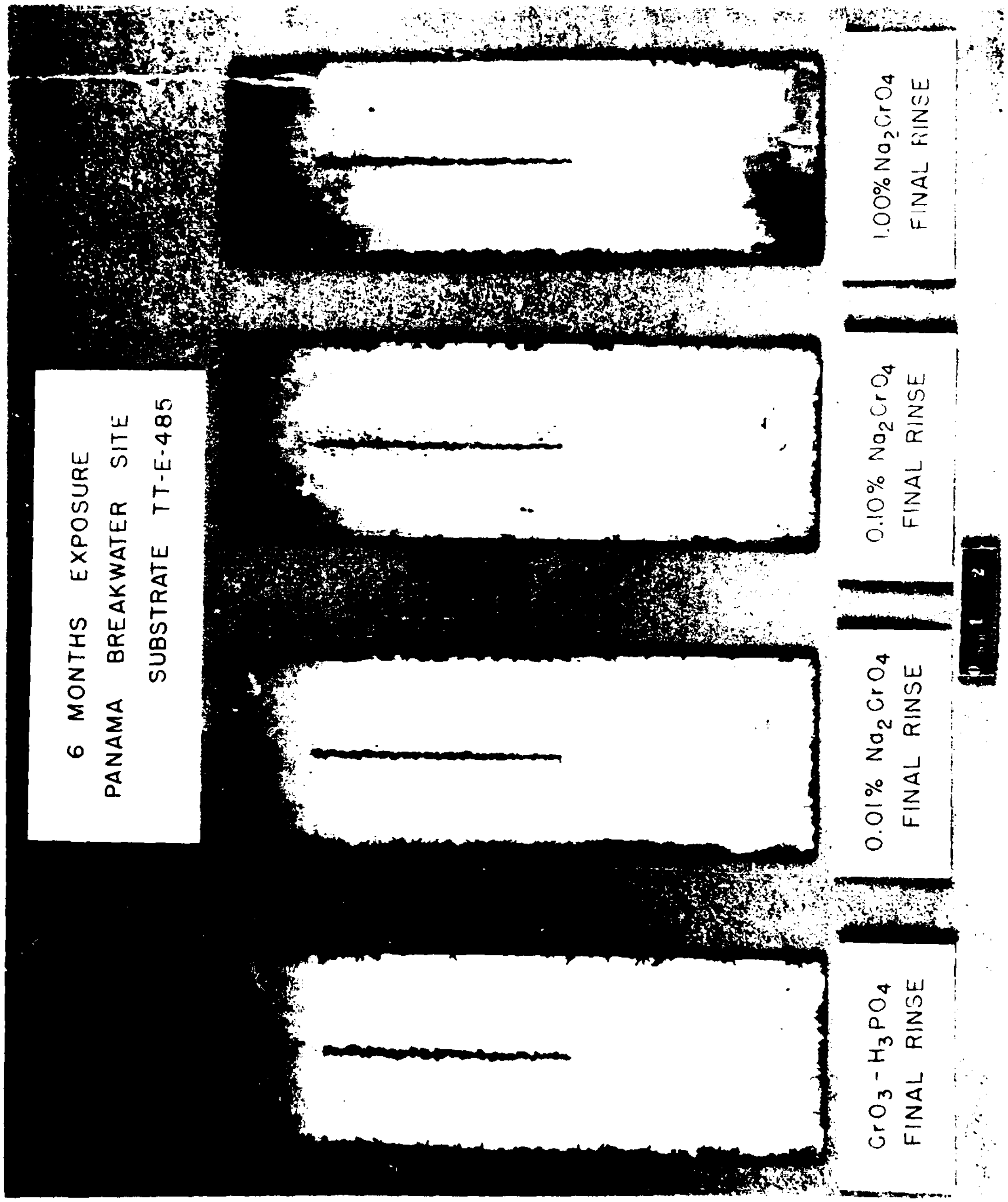
PHOTOGRAPH I



PHOTOGRAPH 2



PHOTOGRAPH 3



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13 ABSTRACT

In an effort to increase corrosion resistance of TT-C-490, Type I, zinc phosphate pretreatments, a study was conducted on inhibitors added to the final rinse. Salt spray testing and tropical exposure studies indicated that a final rinse containing sodium chromate produced an increase in underfilm corrosion resistance with one coat paint systems.